Giant ESR Line in One-Dimensional $(CH_3)_4NMnCl_3$ (TMMC) at Very Low Frequencies

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We report on a new electron-spin-resonance (ESR) effect occurring in one-dimensional systems at very low frequencies. The ESR line is narrowed and enhanced when the chain axis is directed along the linearly oscillating field (perpendicular to the static one). In the ideal case the line becomes singular for $\omega \to 0$. The phenomenon has been observed by measuring ESR absorption in a quasi-one-dimensional $(CH_3)_4NMnCl_3$ sample at frequencies 25 and 225 MHz. This effect is described by Bloch equations with damping on a single spin component, in perfect agreement with a microscopic theory.

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The first electron-spin-resonance (ESR) experiment in the one-dimensional system TMMC[1] $[(CH_3)_4NMnCl_3]$ was performed in 1971. Since that time, the interest in spin dynamics has become manifest by the many theoretical and experimental papers published on this topic. The effects of frequency ω and field orientation on the shape, width, and shift of ESR lines have been studied in various pure[2] and doped[3] quasi-one-dimensional (1D) magnetic systems, TMMC remaining, however, the most popular one.

In this Letter we report on a new effect which occurs at very low frequencies. We show that the ESR line is narrower and more intense for a preferred orientation of the chain axis along the linearly polarized oscillating field $\vec{H}_1$. This feature is more pronounced the lower the frequency ω. It is known[4] that the absorbed power is proportional to ω^2 times the real part $\Gamma_x'(\omega)$ of the Laplace transform of the autocorrelation function $\langle S_x(0)S_x(t)\rangle$. S_x is the total spin component along $\vec{H}_1$, here supposed to be parallel to $\hat{x}$, the static magnetic field $\vec{H}_0$ being directed along the $\hat{z}$ axis. The chain axis $\vec{c}$ is defined by spherical coordinates (θ, ϕ). We show that, for the favorable condition $\theta = 90°$, $\phi = 0°$ (i.e., $\vec{c} \parallel \vec{H}_1$), $\Gamma_x'(\omega)$ reaches a maximum $\langle S_x^2\rangle/2\omega = NS(S+1)/6\omega$, N being the number of ions with spin S in the sample. It would tend towards a delta function at $\omega = 0$ in the ideal case where interchain and hyperfine interactions do not inhibit this phenomenon. This drastic enhancement does not exist for $\vec{c} \perp \vec{H}_1$ and thus a strongly anisotropic behavior can be observed under variation of the chain orientation in the x-z plane.

All of these features have been verified in TMMC by measuring absorption lines at frequencies 25 and 225 MHz at room temperature. The ESR absorption amplitudes are recorded directly (without the use of a synchronous amplifier).

We have been able to perform absolute measurements of Γ_x' by comparing it with the signal produced by a sample of pure diphenylpicrylhydrazyl (DPPH), under the same experimental conditions (see Fig. 1 and Table I). In the latter case the maximum Γ_x' is $N'S'(S'+1)/6\gamma_e\Delta H$, where one takes into account the number N' of spins S' and the half linewidth at half height of the DPPH sample ΔH; γ_e is the gyromagnetic ratio.

A simple explanation of the effect may be given as follows. Let us consider an infinite chain of spins $\vec{S}_i$ coupled by isotropic exchange and dipolar interaction. If the chain axis is in the x direction, parallel to $\vec{H}_1$, the anisotropic part of the dipolar Hamiltonian is $\sum_{i,n} g(n) S_i^x S_{i+n}^x$, where g is a coupling constant, and thus commutes with S_x: It produces no damping. It follows that, for $H_0 = 0$, S_x is a constant of motion and the resonance line is a delta function at $\omega = 0$. For a finite H_0 in the z direction, it is possible to represent the spin motion by Bloch equations, with only one damping constant T_2 for the y total-spin component:

$$\dot{S}_x = -\omega_z S_y, \quad \dot{S}_y = \omega_z S_x - S_y/T_2, \quad \omega_z = \gamma_e H_0.$$

After multiplying each term of the equalities by $S_x(0)$, taking the ensemble average, and making a Laplace transformation, one obtains

$$\Gamma_x'(\omega) = \frac{\langle S_x^2\rangle \omega_z^2/T_2}{(\omega_z^2 - \omega^2)^2 + \omega^2/T_2^2}. \tag{1}$$

In the same way one can obtain the spectrum for $\vec{c} \perp \vec{H}_1$ (the chain axis in the y direction). The result is like (1) but with ω replacing ω_z in the numerator. At high frequencies ($\omega \simeq \omega_z \gg T_2^{-1}$) the lines are the same for the two configurations, with a half-width $1/2T_2$. At low frequencies ($\omega \ll T_2^{-1}$) the behaviors are quite different. For $\vec{c} \parallel \vec{H}_1$ the absorption is zero at zero field and passes through a maximum $\Gamma_{\max}' = \langle S_x^2\rangle/2\omega$, independent

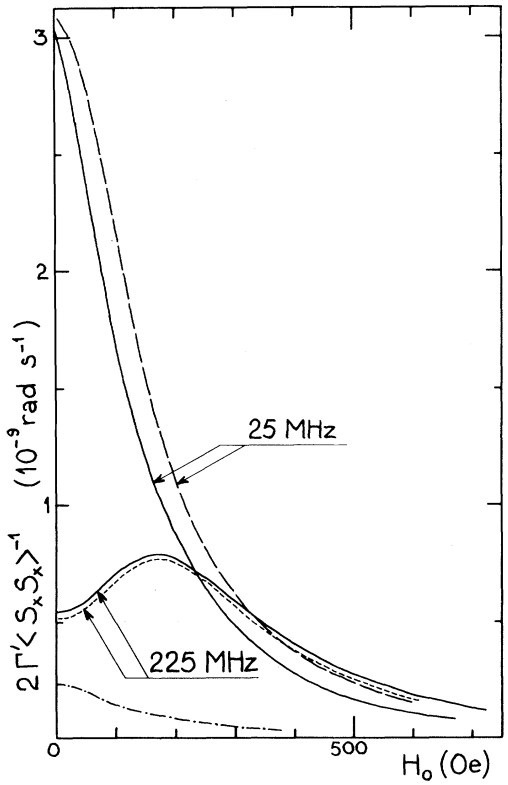

FIG. 1. Absorption lines in TMMC at 300 K. The solid lines are experimental results, the chain axis $\vec{c}$ being directed along the oscillating field $\vec{H}_1$; the dashed lines are theoretical ones. The lower dot-dashed line is the experimental result for $\vec{c} \perp \vec{H}_1$ ($\vec{c} \parallel \hat{y}$), at frequency 25 MHz.

of the strength of the interactions, for a field $\omega_z \simeq (\omega T_2^{-1})^{1/2}$. There is thus a very important resonance shift towards high fields, whose remnant at the X band was studied by Natsume *et al.*[5] For $\vec{c} \perp \vec{H}_1$ the maximum is much smaller: $\Gamma'_{max} \simeq \langle S_x^2 \rangle T_2$. The predicted enhancement is indeed observed (see Fig. 1) but there is a loss of signal amplitude at 25 MHz (about 50%) and furthermore the maximum at this frequency occurs at zero field, in disagreement with Eq. (1). This discrepancy is due to additional interactions such as interchain couplings, spin-lattice relaxation processes, etc., which have been neglected so far and effectively damp S_x. We can accordingly introduce a damping constant for S_x, T_2', which is $\gg T_2$. The main modification to Eq. (1) is to replace ω_z^2 by $\omega_z'^2 = \omega_z^2 + (T_2' T_2)^{-1}$. The line is shifted towards lower fields and its maximum is reduced and occurs at zero field if $\omega < (T_2')^{-1}$. Although the S_x damping considerably modifies the low-field value of Γ'_x and the resonance field, it has negligible effect on Γ'_{max} provided that $\omega > (T_2')^{-1}$. This is verified at 225 MHz, for which one has indeed $\Gamma'_{max} \simeq \langle S_x^2 \rangle / 2\omega$.

The meaning of T_2' appears clearly at zero field. Suppose for example that the static field $\vec{H}_0$ is parallel to the x axis, as $\vec{H}_1$, and the chain axis S_x relaxes towards an equilibrium state with a time constant T_1 related to interchain couplings. It is easily seen that, when H_0 is decreased to zero, T_2' just coincides with the longitudinal relaxation time along the chain $T_1 (H_0 \to 0)$. The zero-field signal for $\vec{c} \parallel \vec{H}_1$ now becomes $\langle S_x^2 \rangle T_1^{-1} / \omega^2 + (T_1^{-1})^2$. Our measurements give a value $T_1^{-1} = 6 \times 10^8$ rad s^{-1}. An X-band measurement[6] of this time along the chain gave the result T_1^{-1} (X band) $= 2 \times 10^8$ rad s^{-1}. The relaxation-rate decrease is due to exchange narrowing.

In Fig. 1 we plot theoretical curves with the damping terms $T_2^{-1} = 10^{10}$ rad s^{-1} and $(T_2')^{-1} = 0.6 \times 10^9$ rad s^{-1}, assumed to be field independent for simplicity. The agreement appears fairly good. Note that the absolute values of Γ'_x, obtained from the DPPH measurements, are given with a precision of $\simeq 10\%$.

Another evidence of the "divergence effect" is given by the anisotropy of the ESR absorption. The chain axis has been varied in the $(\vec{H}_0, \vec{H}_1)$ plane. At 25 MHz the line maximum always occurs at zero field but its value strongly decreases when $\vec{c}$ is moved away from $\vec{H}_1$, while the line broadens. At 225 MHz the same decrease of Γ'_{max} occurs but to a lesser degree. If we measure $\alpha = \Gamma'_{max}(\theta = 90°) / \Gamma'_{max}(\theta = 0°)$, the value of this parameter is about

TABLE I. Comparison of theoretical and experimental Γ'_{max}(TMMC)/Γ'_{max}(DPPH) at two frequencies.

Frequency (MHz)	TMMC mass (g)	DPPH mass (g)	DPPH width ΔH (G)	Theoretical ratio	Experimental ratio
25	5.40	0.23	0.8	42	20
225	1.81	0.21	1.0	2.1	2.35

14 at 25 MHz and 3 at 225 MHz. At $\theta=0°$ no special effect occurs and $\Gamma'_{max}(\theta=0°)$ is almost constant in the frequency range and can be used as a reference. The comparison of the α values is consistent with the results of Table I. On the other hand, if the chain axis is varied in the y-z plane, perpendicular to $\vec{H}_1$, the spectrum exhibits a noticeable feature: All lines have the same zero-field amplitude. This is obvious for the ideal chain, at all ω values, on the basis of axial symmetry. The only relevant parameter is the angle between $\vec{H}_1$ and the chain axis, which remains constant in the y-z plane. In real systems such as TMMC the experiment shows the same behavior, the interchain interactions having in this case a very weak effect, in agreement with our phenomenological model. We have then $\Gamma'_x(\omega_z=0) \simeq \langle S_x^2 \rangle T_2$.

The phenomenological model describes very well the features of the effect but it does not give information on the microscopic origin of the damping rates. Furthermore, the general case with any orientation of the chain axis cannot be described. We have obtained a microscopic theory for the linear chain ESR, which is valid for any frequency and field value and any orientation of the chain axis. The equation of motion of the total spin is solved by means of a memory-function formalism[7,8] with the use of a total-spin projector.[9,10] The results are exact in the limit of linear response and high temperatures. The details of the calculation will be given in a forthcoming paper. It is a remarkable feature that this theory gives *exactly* the same result as the modified Bloch equations for $\vec{c} \parallel \vec{H}_1$ [Eq. (1)] and $\vec{c} \parallel \hat{y}$. The theoretical expression for T_2 contains a function $\phi(\omega)$ which involves time correlations between four localized spins. If we extract the Zeeman modulation (an approximation expected to be valid when isotropic exchange is preponderant[11]), we have

$$T_2^{-1} = \tfrac{9}{8}\omega_D^2[\phi(\omega+\omega_z)+\phi(\omega-\omega_z)]. \qquad (2)$$

with $\omega_D=\hbar\gamma_e^2/c^3$, c being the distance between neighboring ions. $\phi(\omega)$ is the real part[12] of the Laplace transform of

$$\Phi(t) = \sum_{i,j,k,l} |i-j|^{-3}|k-l|^{-3}\langle S_i^+(t)S_j^+(t)S_k^-(0)S_l^-(0)\rangle/\langle S_+S_-\rangle.$$

S_i^+, S_+, etc., are the usual ladder spin operators. The time evolution of the spins is governed by modified[8] exchange and dipolar Hamiltonians. The exchange interaction gives rise to a long-time diffusive process, which can be derived by a decoupling scheme. The dipolar interaction introduces a cutoff at a time $\sim t_c=\omega_c^{-1}$. For the high frequencies it has been assumed,[13] from heuristic arguments, that ω_c is related to the linewidth, so that a self-consistent treatment can be done, in reasonable agreement with experiment.[14] Two simple cases can be considered when the diffusion process is preponderant:

$$\phi(\omega) \propto \omega^{-1/2} \quad \text{for} \quad \omega >> \omega_c$$

and

$$\phi(\omega) \simeq \tfrac{8}{3}Z^2(3)S(S+1)/(2D\omega_c)^{1/2} \quad \text{for} \quad \omega << \omega_c,$$

with $Z(3)=\sum_n n^{-3}$, D being the spin diffusion coefficient. With the TMMC values, and taking into account a small temperature correction,[14] one obtains $\omega_c \sim 2\times10^{10}$ rad s^{-1}. The resulting relatively small field variation of T_2 allows us to understand the good fit between the experimental and theoretical results in Fig. 1.

In conclusion, we have predicted and observed in the archetypal 1D system TMMC a new effect: At low frequencies there is a phenomenon of divergence when the chain axis is parallel to the oscillating field polarization. This "divergence effect" does not require 1D spin diffusion for its existence. However, the two phenomena have partly the same origin: the conservation of total spin. But spin diffusion occurs because isotropic exchange interaction commutes with all components of total spin; the divergence effect occurs when there is an anisotropic term which commutes with a particular component. In this respect, all interactions with axial symmetry, such as Ising and single-ion anisotropy, hold as well as the dipolar, in a linear chain. The 1D spin diffusion has an influence on the strength of the effect since the resulting slow decay of correlation functions gives rise to important values of T_2^{-1}, thus enhancing the effect which goes like T_2^{-1}/ω.

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